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Associate Counsel (Patents)
Code 10082
Naval Research Laboratory
Washington, DC 20375-5000

EXAMINER

SODERQUIST, ARLEN

ART UNIT

PAPER NUMBER

1743

DATE MAILED: 09/16/2005

Please find below and/or attached an Office communication concerning this application or proceeding.

Office Action Summary

Application No.

09/544,344

Applicant(s)

SNOW ET AL.

Examiner

Arlen Soderquist

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-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If the period for reply specified above is less than thirty (30) days, a reply within the statutory minimum of thirty (30) days will be considered timely.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

- 1) ☒ Responsive to communication(s) filed on 10 March 2005.
- 2a) ☐ This action is **FINAL**. 2b) ☒ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

- 4) ☒ Claim(s) 1,2,4-9,21,22,25-38 and 40-51 is/are pending in the application.
- 4a) Of the above claim(s) _____ is/are withdrawn from consideration.
- 5) ☐ Claim(s) _____ is/are allowed.
- 6) ☒ Claim(s) 1,2,4-9,21,22,25-38 and 40-51 is/are rejected.
- 7) ☐ Claim(s) _____ is/are objected to.
- 8) ☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☒ The drawing(s) filed on 06 April 2000 is/are: a) ☒ accepted or b) ☐ objected to by the Examiner.
- Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
- Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

- 12) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☐ All b) ☐ Some * c) ☐ None of:
1. ☐ Certified copies of the priority documents have been received.
2. ☐ Certified copies of the priority documents have been received in Application No. _____.
3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).
- * See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

- 1) ☒ Notice of References Cited (PTO-892)
- 2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
- 3) ☐ Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08)
Paper No(s)/Mail Date _____
- 4) ☐ Interview Summary (PTO-413)
Paper No(s)/Mail Date. _____
- 5) ☐ Notice of Informal Patent Application (PTO-152)
- 6) ☐ Other: _____

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1. Applicant's Notice of Appeal filed March 10, 2005 closed prosecution in this application. In considering the amendment that was filed on the same date, it was noticed that issues unrelated to the amendment were present in the claims rejected in the previous office action. To properly deal with these issues prosecution is being reopened.

2. Claims 5 and 46 are objected to under 37 CFR 1.75(c), as being of improper dependent form for failing to further limit the subject matter of a previous claim. Applicant is required to cancel the claim(s), or amend the claim(s) to place the claim(s) in proper dependent form, or rewrite the claim(s) in independent form. Claim 1 limits the tail structure to a group that does not include a primary aliphatic moiety (group) as the functional group. Thus these claims are outside of the scope of claim 1. Due to the presence of these claims, claim 1 will be treated with art that would include the presence of primary alkanes in the encapsulating ligand shell.

3. Claims 1-2, 4-9, 21-22, 25-38 and 40-51 are rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention. Each of the independent claims contains the following phrase "the tail having a structure and composition designed to provide additional stabilization of metal clusters against irreversible agglomeration" in the language describing the properties of the ligand shell. Page 8, lines 11-13 teach that a particle is typically "stabilized" by the metal core being effectively encapsulated by the ligand shell. Page 14, line 18 to page 15, line 1 teach that it is important for the ligand to have a strong interaction with the neutral metal core to prevent the metal core from coagulating and being able to be redispersed. In this section sulfur compounds and amines are specifically exemplified as providing this strong interaction. Thus it is not clear if the above language regarding the tail structure prevents a bifunctional molecule such as the claimed heterofunctional group from having either the sulfur or amine functionality. It is also not clear if this language excludes a three dimensional structure using the dithiol linking molecules since these molecules are found in the encapsulating ligand shell and clearly promote the irreversible agglomeration of the particles (see page 18, line 24 to page 19, line 2). In the alternative, it is not clear if only some of the molecules in the encapsulating ligand shell are required to be of the type that provides stabilization against irreversible agglomeration while the presence of some molecules that promote the agglomeration is within the scope of the above language. Since claim 29 and those that depend therefrom are drawn to a method that

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produces a structure that would be excluded by the first interpretation, the claims will be examined as only requiring some of the ligand molecules in the ligand shell have the required structure. There is a particular question as to the allowed scope of the tail functional group in claims 37 and 50 in that they specifically recite a functional group, NH₂, that the instant specification acknowledges as having a strong interaction with the metal core (promotes agglomeration). In claims 2 and 22 it is not clear if the alloy of "two or more such metals" is limited to those specifically listed in the body of the claims or includes other metals that are not specifically listed. In claims 41 and 47 it is not clear if the "araliphatic" term used finds antecedent basis in the aromatic group of claim 1. A broad range or limitation together with a narrow range or limitation that falls within the broad range or limitation (in the same claim) is considered indefinite, since the resulting claim does not clearly set forth the metes and bounds of the patent protection desired. See MPEP § 2173.05(c). Note the explanation given by the Board of Patent Appeals and Interferences in *Ex parte Wu*, 10 USPQ2d 2031, 2033 (Bd. Pat. App. & Inter. 1989), as to where broad language is followed by "such as" and then narrow language. The Board stated that this can render a claim indefinite by raising a question or doubt as to whether the feature introduced by such language is (a) merely exemplary of the remainder of the claim, and therefore not required, or (b) a required feature of the claims. Note also, for example, the decisions of *Ex parte Steigewald*, 131 USPQ 74 (Bd. App. 1961); *Ex parte Hall*, 83 USPQ 38 (Bd. App. 1948); and *Ex parte Hasche*, 86 USPQ 481 (Bd. App. 1949). In the present instance, claims 47-48 recite the broad recitations araliphatic mercaptan and dithiol respectively, and the claims also recite specific molecules which are the narrower statement of the range/limitation.

4. The following is a quotation of the first paragraph of 35 U.S.C. 112:

The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same and shall set forth the best mode contemplated by the inventor of carrying out his invention.

5. Claims 1-2, 4-9, 21-22, 25-38 and 40-51 are rejected under 35 U.S.C. 112, first paragraph, because the specification, while being enabling for a device having the multiplicity of particles in three-dimensional close-packed orientation made by the process of claim 28, does not reasonably provide enablement for a three dimensional structure made by a process other than the spraying process of claim 28. The specification does not enable any person skilled in the art to which it

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pertains, or with which it is most nearly connected, to make and use the invention commensurate in scope with these claims. The above noted clarity problems regarding "the tail having a structure and composition designed to provide additional stabilization of metal clusters against irreversible agglomeration" language appears to exclude the layer by layer method and the three dimensional structures produced thereby. Page 17, lines 9-11 teach that a method of casting from solution followed by slow evaporation does not produce an acceptable film. See page 17, line 8 through page 19, line 2 of the instant specification for the only methods for forming the multiplicity of particles in three-dimensional close-packed orientation that are taught in the specification. Applicant and the art of record do not teach any other manner of making the particles in three-dimensional close-packed orientation. Thus, the three methods taught in the instant specification, only the spraying method appears to be within the "irreversible agglomeration" language of the claims.

6. In the rejections that follow, examiner will be citing portions of the instant specification to show that various claimed properties are inherent or found in the teachings of the applied references. The format used will be bold italicized letters contained within parentheses.

7. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

The factual inquiries set forth in *Graham v. John Deere Co.*, 383 U.S. 1, 148 USPQ 459 (1966), that are applied for establishing a background for determining obviousness under 35 U.S.C. 103(a) are summarized as follows:

1. Determining the scope and contents of the prior art.
 2. Ascertaining the differences between the prior art and the claims at issue.
 3. Resolving the level of ordinary skill in the pertinent art.
 4. Considering objective evidence present in the application indicating obviousness or nonobviousness.
8. Claims 1-2, 4-5, 7-9, 21-22, 25-27, 33-34, 37-38, 40-41, 46-47 and 49-51 are rejected under 35 U.S.C. 103(a) as being unpatentable over Bethell (*J. Electroanal. Chem.*) in view of Nakanishi or Hostetler (both newly cited and applied). In the paper Bethell describes simple

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methods for the production of Au nanoparticles with narrow size distributions by reduction of tetrachloroaurate solutions in the presence of thiol-containing organic compounds which self-assemble on the Au surface. Stable solutions of somewhat larger particles can be produced if the thiol is absent. The thiol-derivatized materials are stable in air over long periods and can be handled in much the same way as simple organic compounds. Page 138, column 1, last full paragraph teaches derivatized particles having a core diameter of 1.5-3 nm with particles that are derivatized with nonanethiol having a mass suggesting a gold content of about 150 atoms. Subheading 2.1 contains a reference to an article by M. Brust that is also cited in the instant specification as one of the methods for making the metal core-ligand particles of the instant invention (*see page 13, line 23 to page 14, line 8*). In figure 1(b) a spectrum of dodecanethiol-derivatized particles is presented (*see examples 10-13, page 33 line 9 to page 34, line 10 for a description of particles made with dodecanethiol*). Table 1 teaches a range of dithiol containing molecules. Each of these is clearly within the thiol derivatives taught in the instant specification (*see page 12 line 21 to page 13 line 11 and 26-30 page 39, line 12 to page 41, line 23*). Using dithiols as the derivatizing spacer units, methods were developed for the preparation of materials in 3-dimensional form and as thin films attached to a solid substrate (figure 3, and the only full paragraph on page 139). (*A comparison of this procedure with that found in examples 26-30 shows that there is significant similarity and that the Bethell process forms a self-assembled layered structure as in the examples.*) Such materials show conductivities that mimic the behavior of semiconductors and that depend markedly on the structure of the dithiol used to link the Au particles together. Thus there is inherently a structure capable of being used to measure conductivity. The increase in conductivity with increasing temperature probably involves activated electron hopping from particle to particle. Surfaces treated with a coating of the materials show electreflectance changes with applied potential that also differ according to the structure of the dithiol spacer. Unusual effects were observed on heterogeneous electron transfer from electrode surfaces treated with layers of the Au nanoparticles and dithiol spacers. Applications for these nanostructured materials can be envisaged, which range from submicroelectronic devices and circuitry to electrical modification of the reflectance of glass. Such applications will require a multidisciplinary approach with a substantial organic chemical research input. Section 4 and figure 5 discuss other methods of making the clusters which use

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multi-functional groups on the ligand layer surrounding the metal core. *(Additional sections of the instant specification that are relevant to the inherency of the Bethell structure are page 13, lines 16-18 teaching that the thickness of the ligand shell is determined by the size of the ligand molecule and page 24, lines 15-25 showing that ligand shell thickness on particles made with of alkanethiols having 6, 8, 12 or 16 carbons, C6, C8, C12 and C16, are 0.71 nm, 0.86 nm, 1.16 nm and 1.58 nm, respectively. This clearly shows that the thickness of the ligand shell of the particles is anticipated by the Bethell reference due to the use of similar compounds to synthesize the self assembled materials in a similar manner.)* Bethell does not teach a three dimensional structure having particles with both ligands that do not interact with other metal particles and ligands that link two particles together.

In the paper Nakanishi teaches that layer-by-layer self-assembly of composite thin films of Cd sulfide (CdS) nanoparticle and alkanedithiol was achieved on a Au substrate by an alternate immersion into solutions of dithiols (1,6-hexanedithiol and 1,10-decanedithiol) and a solution containing CdS nanoparticles (~3 nm in diameter). The layer-by-layer structure was confirmed by angle-resolved XPS at each composite-film preparation step. The proposed structure and mechanism of self-assembly were in agreement with previous results obtained by FTIR reflection-absorption spectroscopy. Figure 1 and the experimental section teach that the CdS colloids were prepared with a molecule that was at least partially replaced by the dithiol linking agent used.

Hostetler discusses monolayers in three dimensions, the synthesis and electrochemistry of ω -functionalized alkanethiolate-stabilized gold cluster compounds. They report the synthesis and characterization of Au cluster compounds containing a mixture of alkanethiolate and ω -substituted alkanethiolate ligands. Cluster molecules prepared with alkanethiolate ligands, according to previous work, have a ~1.2 nm radius Au core that, modeled as a 309-Au atom cubooctahedron, bears a monolayer ligand skin of ~95 alkenethiolate chains. The ω -functionalized clusters are synthesized by place exchange reactions in solution mixtures of alkanethiolate cluster molecules and ω -substituted alkanethiols, where the ω -substituent can be -Br, -CN, vinyl, or ferrocenyl. The second paragraph of page 4212 teaches that this is done in this manner because it preserves the gold core dimensions that occur with other functionalization

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schemes. Hostetler references two articles by Brust that are also referenced by Bethell. The reaction products, according to ^1H NMR spectroscopy, include cluster molecules with as many as 44 bromide and 15 ferrocenyl ω -substituents. Steric ω -substituent interactions appear to constrain the extent of place exchange. Ferrocenyl-substituted clusters are electroactive in methylene chloride solutions as adsorbed monolayers and as diffusing solutes. The mass transport behavior indicates that as many as 15 ferrocene units in a substituted cluster molecule can be oxidized at an electrode surface over a potential range as narrow as that required to oxidize a ferrocene monomer, i.e., the cluster has promise as a reagent that delivers multiple equivalents of redox activity at nearly identical formal potentials. The Au cores of the clusters also exhibit "double layer" charging behavior and are thus true molecular "nanoelectrodes".

It would have been obvious to modify the procedure for making three-dimensional structures of Bethell to use particles having an encapsulating shell and exchanging them as taught by Nakanishi or Hostetler with the linking molecule because of the ability to preserve the metal core diameter as taught by Hostetler compared to other linking methods.

9. Claims 2, 4, 6, and 22 are rejected under 35 U.S.C. 103(a) as being unpatentable over Bethell in view of Nakanishi or Hostetler as applied to claims 1 and 22 above, and further in view of Natan (US 5,609,907). Bethell does not teach other types of metal colloids or the use of amine functions in the coating materials.

In the patent Natan teaches the formation of self-assembled metal colloid layers. Figure 1A with its associated discussion teach that the colloids can be gold, silver or other suitable metals. Column 3, lines 39-59 and the brief description of Figures 1A and 1B teach the additional use of amine and other functional groups in addition to thiols used to immobilize the colloids on a surface. The brief discussion of the figures also includes colloids having two layers of metal. Figure 1D shows the various levels of self-assembled colloids including multilayered (bulk).

It would have been obvious to one of ordinary skill in the art at the time the invention was made to incorporate the metal cores and metal interacting functional groups of Natan into the self-assembled colloid structures of Bethell because as shown by Natan the specifically claimed metals and functional groups would have been recognized as functional equivalents to those of Bethell relative to the formation of the self assembled colloid layers.

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10. Claims 27, 29-32, 43-45 and 48 are rejected under 35 U.S.C. 103(a) as being unpatentable over Bethell in view of Nakanishi or Hostetler as applied to claims 1-2, 4-5, 7-9, 21-22, 25-27, 33-34, 37-38, 40-41, 46-47 and 49-51 above, and further in view of Terrill and Andres. Bethell does not teach the type of electrode used or the measurement equipment used.

In the paper Terrill (*cited in the instant specification on page 26, lines 9-12*) discusses NMR, SAXS, Thermal, and Electron Hopping Studies of alkanethiol stabilized gold cluster monolayers in three dimensions. Au clusters stabilized by chemisorbed monolayers of octane-, dodecane-, or hexadecanethiolate were studied in solution and in the solid phase. These materials can be pumped free of solvent to form a dark brown solid that can be re-dissolved in nonpolar solvents. Their exceptional stability suggests that they may be viewed as cluster compounds. The self-assembled alkanethiolate monolayers stabilizing the metal clusters can be studied by using techniques that are insufficiently sensitive for study of a monolayer on a flat surface (e.g., ^1H and ^{13}C NMR, elemental analysis, DSC, thermogravimetry (TGA), diffusion-ordered NMR spectroscopy (DOSY)). Results from such measurements (combined with SAXS data on solutions of the clusters and AFM and STM images) are consistent with a small, monodisperse (12 Å radius) Au core, which modeled as a sphere contains ~ 400 Au atoms and ~ 126 alkanethiolate chains, or if modeled as a cuboctahedral structure contains 309 Au atoms and ~ 95 alkanethiolate chains. High-resolution NMR spectra of cluster solutions display well-defined resonances except for methylenes nearest the Au interface; the absence of the latter resonance is attributed to a combination of broadening mechanisms based on the discontinuous change in magnetic susceptibility at the metal-hydrocarbon interface and residual dipolar interactions. Films of the dry, solid cluster compound on interdigitated array electrodes (see pages 12538-12539, experimental section for preparation and measurements) exhibit current-potential responses characteristic of electron hopping conductivity in which electrons tunnel from Au core to Au core. The electron hopping rate decreases and the activation barrier increases systematically at longer alkane chain length. The results are consistent with electron transport rate control being a combination of thermally activated electron transfer to create oppositely charged Au cores (cermet theory) and distance-dependent tunneling ($\beta = 1.2\Delta^{-1}$)

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through the oriented alkanethiolate layers separating them. See pages 12545 - 12548 for a discussion of the electrical measurements.

In the paper Andres teaches self-assembly of a two-dimensional superlattice of molecularly linked metal clusters. Close-packed planar arrays of nanometer-diameter gold clusters that are covalently linked to each other by rigid, double-ended organic molecules were self-assembled. Au nanocrystals, each encapsulated by a monolayer of alkyl thiol molecules were cast from a colloidal solution onto a flat substrate to form a close-packed cluster monolayer. Organic interconnects (aryl dithiols or aryl diisonitriles) displaced the alkyl thiol molecules and covalently linked adjacent clusters in the monolayer to form a two-dimensional superlattice of metal quantum dots coupled by uniform tunnel junctions. Electrical conductance through such a superlattice of 3.7-nm-diameter Au clusters, deposited on a SiO₂ substrate in the gap between two Au contacts and linked by an aryl di-isonitrile [1,4-di(4-isocyanophenylethynyl)-2-ethylbenene], exhibited nonlinear Coulomb charging behavior. Page 1692 in the two paragraphs that bridge the three columns, ligand shell thickness of ~1.2 nanometers are taught for the dodecanethiol ligand shell along with the possibility that the molecules on adjacent clusters interpenetrate to give a cluster spacing that is less than the expected layer thickness. For the dithiol linked clusters the spacing is about 1.7 nm between clusters using a 2 nm length molecule as the linking molecule. In the last full paragraph of the center column of page 1691, Andres teaches that the synthetic method used produces particles that are equivalent to those produced by the Brust method (see reference 5). The advantage of using the Andres method is flexibility in the formation of the particles.

It would have been obvious to one of ordinary skill in the art at the time the invention was made to incorporate the electrodes and measurement apparatus of Terrill into the formation method of Bethell because of their known use and sensitivity for measuring resistivity of self-assembled colloid clusters as shown by Terrill. It also would have been obvious to one of ordinary skill in the art at the time of the invention to use the ligand displacement method of forming the linked clusters as taught by Andres in producing the layered structure of Bethell because of the greater flexibility in synthesis as taught by Andres

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11. Applicant's arguments with respect to the claims have been considered but are moot in view of the new ground(s) of rejection.

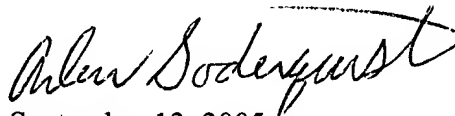
12. Claims 28, 35-36 and 42 are objected to as being dependent upon a rejected base claim, but would be allowable if rewritten to overcome the rejection(s) under 35 U.S.C. 112, second paragraph, set forth in this Office action and to include all of the limitations of the base claim and any intervening claims. The art of record fails to teach or suggest the claimed combination or elements. Relative to claims 35-36, it is noted that although the respective elements are conventional as evidenced by the page 21, line 17 to page 22, line 8, examiner was not able to determine if they are part of the measurement apparatus taught by Terrill.

13. The prior art made of record and not relied upon is considered pertinent to applicant's disclosure. The additionally cited art relates to formation of metal clusters or particles.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Arlen Soderquist whose telephone number is (571) 272-1265. The examiner's schedule is variable between the hours of about 6:30 AM to about 5:00 PM on Monday through Thursday and alternate Fridays.

A general phone number for the organization to which this application is assigned is (571) 272-1700. The fax phone number to file official papers for this application or proceeding is (571) 273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).



September 13, 2005

ARLEN SODERQUIST
PRIMARY EXAMINER